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Molecular Kohn-Sham exchange-correlation potential from the correlated *ab initio* electron density

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The molecular Kohn-Sham (KS) exchange-correlation potential v_{xc} has been constructed for LiH from the correlated *ab initio* density ρ by means of the simple iterative procedure developed by van Leeuwen and Baerends [Phys. Rev. A **49**, 2421 (1994)]. The corresponding KS energy characteristics, such as the kinetic energy of noninteracting particles T_s, kinetic part of the exchange-correlation energy T_c, and energy of the highest occupied molecular orbital ϵ_N, have been obtained with reasonable accuracy. A relation between the form of v_{xc} and the electronic structure of LiH has been discussed. Test calculations for the two-electron H_2 molecule have shown the efficiency of the procedure.

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I. INTRODUCTION

Modern density-functional theory (DFT) and its numerous applications are essentially based on the Kohn-Sham (KS) one-electron approach [1–3]. A key feature of this approach is the exchange-correlation potential v_{xc}, which represents the local effect of electron exchange and Coulomb correlation in the one-electron KS equations (Hartree atomic units will be used throughout the paper)

$$\{-\tfrac{1}{2}\nabla^2+v_{ext}(\vec{r})+v_H(\vec{r})+v_{xc}(\vec{r})\}\phi_i(\vec{r})=\epsilon_i\phi_i(\vec{r}) , \quad (1)$$

$$\sum_{i=1}^{N}|\phi_i(\vec{r})|^2=\rho(\vec{r}) . \quad (2)$$

Here v_{ext} is the external potential, v_H is the Hartree potential of the electrostatic electron repulsion, N is the number of electrons in the system, and occupied KS orbitals ϕ_i yield the electron density ρ.

Examples of accurate v_{xc} obtained for certain atoms and molecules are of importance for the analysis of electron interaction, and they can also serve as a benchmark for efficient DFT approximations. With orbitals ϕ_i one can calculate a basic KS kinetic functional, the kinetic energy of noninteracting particles T_s,

$$T_s=-\tfrac{1}{2}\sum_{i=1}^{N}\int\phi_i^*(\vec{r}_1)\nabla^2\phi_i(\vec{r})d\vec{r} . \quad (3)$$

Note also that an energy ϵ_N of the highest occupied KS orbital ϕ_N delivers the ionization energy I_p of the system [4–7]

$$\epsilon_{N\sigma}=-I_p . \quad (4)$$

In DFT v_{xc} is defined as a functional derivative of the exchange-correlation energy $E_{xc}[\rho]$ with respect to the density $\rho(\vec{r})$,

$$v_{xc}([\rho];\vec{r})=\frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})} . \quad (5)$$

Since the exact functional form of $E_{xc}[\rho]$ is not known, the same is true for the functional $v_{xc}([\rho];\vec{r})$, so that one cannot use definition (5) to construct an accurate v_{xc}. However, several methods were proposed [8–15] to construct v_{xc} numerically, using essentially accurate ρ (usually, ρ from *ab initio* calculations). Hitherto, all these methods have been applied only to few-electron atomic systems.

This paper presents v_{xc} constructed from the correlated *ab initio* ρ for the LiH molecule, an example of an exchange-correlation potential for a molecule with more than two electrons. KS energy characteristics calculated for LiH, namely T_s, ϵ_N, and the kinetic part of the exchange-correlation energy T_c, are also presented and discussed. The molecular application became feasible because we use a simple and yet efficient method [14] to construct v_{xc}. The method is tested for the two-electron H_2 molecule, since in the special case of $N=2$ one can obtain v_{xc} for a given ρ in a straightforward way [16–18].

II. METHOD

According to [14], v_{xc} corresponding to a given density ρ is calculated with an iterative procedure, starting from some initial guess v_{el}^0 for the effective potential of electron interaction v_{el},

$$v_{el}(\vec{r})=v_H(\vec{r})+v_{xc}(\vec{r}) . \quad (6)$$

At mth iteration, KS equations (1) are solved with the potential v_{el}^m,

$$v_{el}^m(\vec{r})=f^m(\vec{r})v_{el}^{m-1}(\vec{r}) , \quad (7)$$

calculated from the v_{el}^{m-1} of the previous iteration with the correlation factor f^m, the latter being a ratio of the density ρ^{m-1} from the $(m-1)$th iteration and a given ρ,

$$f^m(\vec{r})=\frac{\rho^{m-1}(\vec{r})}{\rho(\vec{r})} . \quad (8)$$

Then ρ^{m-1} in (8) is replaced with ρ^m obtained in mth

iteration, and this procedure continues unless further iterations cease lowering the difference $|\rho^m(\vec{r})-\rho(\vec{r})|$ in the region of nonvanishing densities. Finally, v_{xc} is obtained by subtracting out the Hartree potential $v_H([\rho];\vec{r})$ from the resulting potential (7).

As was pointed out in [14], this iterative procedure is not guaranteed to converge. However, if it converges, then its limit is unique, as guaranteed by the Hohenberg-Kohn theorem applied to a noninteracting electron system [19]. In our calculations we use a slightly modified form of (8),

$$f^m(\vec{r})=\frac{\rho^{m-1}(\vec{r})+a}{\rho(\vec{r})+a}\ , \tag{9}$$

with $a=0.5$, which smooths out an effect of the remote exponential density tails on the procedure.

Correlated ρ for this procedure has been obtained with singly and doubly excited configuration interaction (SDCI) calculations of the ground states of H_2 and LiH at equilibrium distances $R(\text{H–H})=1.401$ a.u. and $R(\text{Li–H})=3.016$ a.u. A basis of contracted Gaussian functions has been used with five s- and two p-type functions for H [20,21] and seven s- and four p-type functions for Li [20]. An extra d-type Gaussian with the exponent $\alpha=1.0$ was added onto each nucleus. The SDCI with this basis recovers 95% of the conventional exact Coulomb correlation energy E_c^e [20] for H_2 and 86% of E_c^e for LiH. Construction (1), (6)–(9) of v_{xc} has been performed in the same basis of molecular orbitals as SDCI calculations of ρ with the specialized density-functional extension [17,22] of the *ab initio* ATMOL package [23]. Matrix elements of v_{el}^m with the basis have been calculated using a numerical integration with grids according to Ref. [24]. Test calculations for H_2 and results for LiH will be presented in the following sections.

III. RESULTS FOR H_2

H_2 provides a good molecular test for the procedure of the preceding section, because for the special case of two-electron closed-shell systems v_{xc} can be obtained in an alternative, straightforward way. In this case there is only one occupied KS orbital ϕ_1, so that an accurate v_{xc} is obtained directly from (1) by the replacement of ϕ_1 in (1) by $(\rho/2)^{1/2}$ [17]. Figure 1 displays v_{xc} for H_2 obtained in this way in [17] from the same SDCI ρ. v_{xc} is plotted in a number of points along the bond axis as a function of the distance z from the bond midpoint.

One can also directly calculate T_s of Eq. (3) from ρ, because for $N=2$ T_s is equal to the von Weizsacker kinetic energy of the system T_W [25],

$$T_W[\rho]=\tfrac{1}{8}\int\frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})}d\vec{r}\ . \tag{10}$$

Furthermore, in this case exchange must precisely cancel the spurious self-interaction of electrons, so that the exchange part v_x of v_{xc} is known and is equal to $-\frac{1}{2}$ of the Hartree potential

$$v_x([\rho];\vec{r})=-\tfrac{1}{2}v_H([\rho];\vec{r})\ . \tag{11}$$

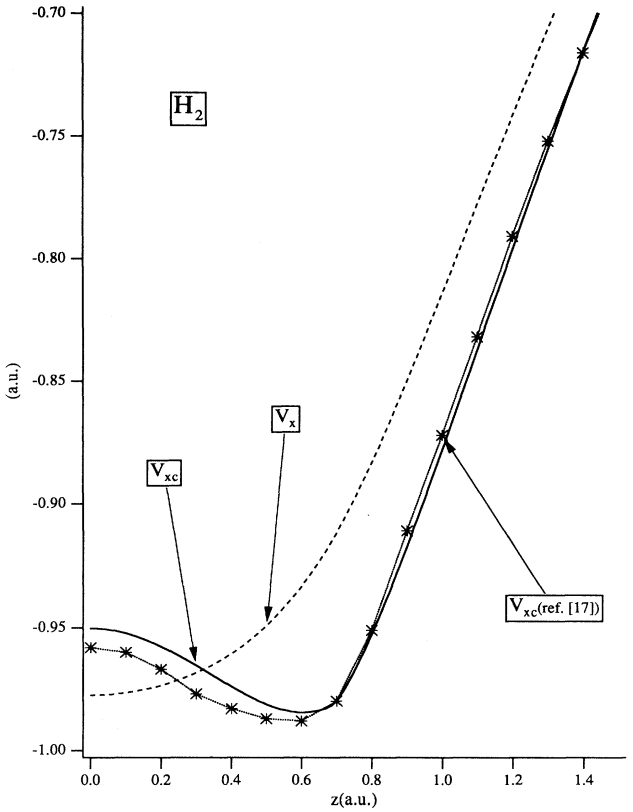

FIG. 1. Comparison of the exchange-correlation potentials constructed for H_2 via procedures [14] and [17] with the exchange potential. Potentials are plotted along the bond axis as functions of the distance z from the bond midpoint. The H nucleus is at $z=0.7005$ a.u.

v_x is also displayed in Fig. 1.

To construct v_{xc} with the iterative procedure, the exchange potential (11) has been used as an initial guess for v_{xc} in (6), which, when combined with $v_H([\rho];\vec{r})$, yields the starting initial potential $v_{el}^0=\frac{1}{2}v_H$. After 45 iterations the procedure (1),(6)–(9) has reached its saturation state, with no further discernible change of results. A good quality of the iteratively obtained KS solution is characterized by the value $T_s=1.140$ a.u. calculated with the resulting KS orbital ϕ_1, which coincides (with all digits included) with that of T_W [Eq. (10)] calculated with correlated ρ. The corresponding orbital energy $\epsilon_1=-0.598$ a.u. is close to minus the ionization energy $I_p=0.603$ a.u. obtained with the same basis by ΔSDCI calculations of H_2 and H_2^+ [17]. In iterations a quality of the density $\rho(\vec{r})=|\phi_1(\vec{r})|^2$ was checking in the region $z<2.0$ a.u., and in this region the density obtained agrees with the correlated ρ within 0.03%.

In Fig. 1 v_{xc} constructed with the iterative procedure is compared with that obtained in a straightforward way [17] and with v_x. Both potentials v_{xc} remain close to each other at all distances, and the corresponding difference does not exceed 0.01 a.u. We have not been

able to converge our KS potential and density to higher accuracy with the present procedure. It appears to be somewhat difficult in general to achieve high numerical accuracy in the KS potential [9,12,14,15]. Anyway, the effect of Coulomb correlation manifests itself in a qualitatively different behavior of v_x and v_{xc}. The former is a monotonic function of z with the minimum at $z=0$, while the latter has a local maximum at $z=0$ and the minimum at $z=0.6$ a.u. It is interesting to note that all potentials appear to have no special point at the H nucleus ($a=0.7005$ a.u.). At longer z all potentials approach to the same Coulombic asymptotics $-1/z$.

From this comparison one can see that starting from a pure exchange potential v_x in the initial guess for (6), the procedure manages to take into account properly the Coulomb correlation effect and to build up a v_{xc} of proper form. To sum up, test calculations for the H_2 molecule show that the iterative procedure of Sec. II provides a reasonable KS solution for the correlated ρ and produces an adequate v_{xc}.

IV. RESULTS FOR LiH

To obtain the KS potential from a correlated ρ for LiH, the following potential v_{xc}^0 has been used as an exchange-correlation part of the initial t_{el}^0:

$$v_{xc}^0([\rho];\vec{r})=v_{X\alpha}(\rho;\vec{r})+2\epsilon_x^B(\rho,\nabla\rho;\vec{r})+2\epsilon_c^{VWN}(\rho;\vec{r}) \ . \tag{12}$$

In (12) $v_{X\alpha}$ is the exchange-correlation $X\alpha$ potential [26], ϵ_x^B is the exchange-energy density-gradient correction of Becke [27], and ϵ_c^{VWN} is the local-density approximation (LDA) of Vosko, Wilk, and Nusair [28] for the correlation energy density. The potential (12) has a proper long-range Coulombic asymptotics $v_{xc}^0 \to -1/|\vec{r}|$, and, based on our previous experience with potential approximations [29,30], we can consider it as a fair initial guess for v_{xc}. The results only insignificantly depend on the value of the parameter α of $v_{X\alpha}$, and the quickest convergence has been achieved with $\alpha=1.1\alpha_{LDA}=0.73$.

The iterative procedure provides a reasonably accurate KS solution for the correlated ρ of LiH. In the iterations the quality of the calculated density has been checked within spheres of radius of 1.6 a.u. around each nucleus, and in this region the density obtained agrees with the SDCI ρ within 0.09%. The energy of the highest occupied KS orbital $\epsilon_2=-0.283$ a.u. coincides (with all digits included) with the experimental ionization energy [31] taken with the opposite sign. The calculated value of the kinetic functional $T_s=7.992$ a.u. is (as it should be) in between the value of the functional (10) $T_W=7.682$ a.u., and the SDCI kinetic energy $T_{SDCI}=8.046$ a.u.

The corresponding kinetic part of the exchange-correlation energy $T_c=T_{SDCI}-T_s=0.054$ a.u. accounts for 76% of minus the total correlation energy of SDCI $E_c^{SDCI}=-0.0712$ a.u. This result corresponds nicely to that obtained with an alternative procedure [32] for the

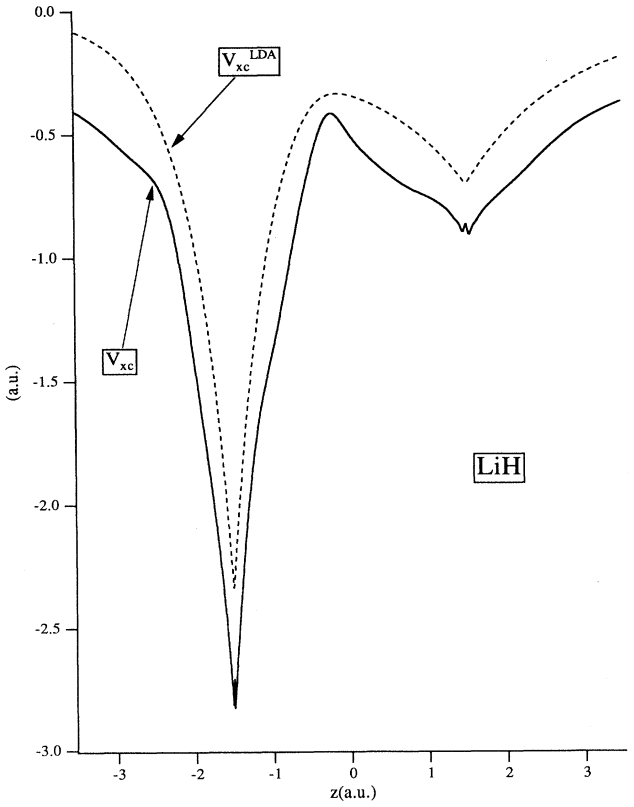

FIG. 2. Exchange-correlation potential and its LDA approximation along the bond axis of LiH as functions of the distance z from the bond midpoint. The Li nucleus is at $z=-1.508$ a.u. and H is at $z=1.508$ a.u.

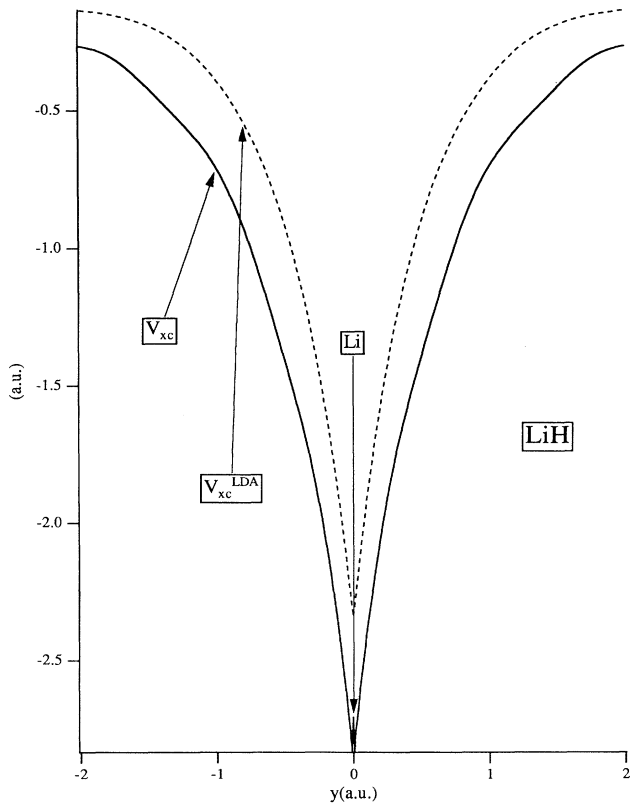

FIG. 3. Exchange-correlation potential and its LDA approximation along the axis perpendicular to the bond axis and going through the Li nucleus.

Be atom, a system with the same number of electrons $N=4$ as in LiH. According to [32], for Be T_c accounts for 78% of $-E_c$, a slightly larger percentage than for LiH. One can anticipate this trend, since Be is, of course, closer than LiH to the limiting case of a tightly bound closed-shell atom, for which $T_c=-E_c$ [33]. Bearing in mind that our SDCI calculations recover 86% of the conventional exact $E_c^e=-0.083$ a.u. [20], we can infer from our results an estimate of $T_c^e=0.063$ a.u. for the accurate value of this functional.

In Figs. 2–5 v_{xc} for LiH is presented as the first example of a molecular Kohn-Sham exchange-correlation potential constructed from the correlated ρ for a system with $N>2$. To provide a reference point, it is compared with the exchange-correlation potential of LDA, v_{xc}^{LDA}, calculated self-consistently with the same basis as v_{xc}.

In Fig. 2 v_{xc} is plotted along the bond axis as a function of a distance z from the bond midpont. Unlike v_{xc} for H_2 (see Fig. 1), v_{xc} for LiH displays a cusplike behavior near both of the nuclei. A similar behavior was also established for atomic v_{xc} and it is considered to be an effect of Coulomb correlation, since the exchange part of v_{xc} should have a smoother, bell-like form in this region [34]. Small positive countercusps at the nuclei (see Fig. 2) are probably artifacts that can possibly be attributed to a deficiency of the Gaussian basis set for the density representation at the nucleus. Of course, it can also be a minor artifact of the iterative procedure of v_{xc} construction. Analogous and sometimes even more pronounced countercusps were also observed for atomic v_{xc} constructed with alternative procedures [9,10]. In any case, it seems to be a minor detail, which does not influence the overall good quality of the results. The absolute minimum of v_{xc} near the Li nucleus, $v_{xc}^{min}(\mathrm{Li})=-2.83$ a.u., is placed in between the corresponding values $v_{xc}^{min}(\mathrm{Li})=-2.3$ a.u. for the neutral Li atom and $v_{xc}^{min}(\mathrm{Li})=-3.2$ a.u. for a Li^+ cation obtained in [9]. However, a local minimum of v_{xc} near the H nucleus $v_{xc}^{min}(\mathrm{H})=-0.91$ a.u. is placed in between $v_{xc}^{min}(\mathrm{H})=-0.77$ a.u. for a H^- anion [18] and the absolute minimum $v_{xc}^{min}(\mathrm{H_2})=-0.98$ a.u., for H_2 molecule (see Fig. 1). This trend clearly reflects the ionic nature of the bond $Li^{\delta+}$—$H^{\delta-}$.

In the bond region v_{xc} exhibits a pronounced peak with a maximum at $z=-0.22$ a.u., which coincides with a saddle point of $\rho(\vec{r})$. The shell structure of LiH is reflected in a clear change of the slope of v_{xc} at the $1s,2s$ boundary at $z=-2.3$ a.u. At longer distances v_{xc} approaches the Coulombic asymptotics. The form of v_{xc}^{LDA} is, in general, similar to that of v_{xc}, a fact that can explain the rather good quality of the electron density reported for LDA calculations and the success of the post-LDA approach. Note, however, that v_{xc}^{LDA} is always an appreciably less attractive potential than v_{xc}; the structure of

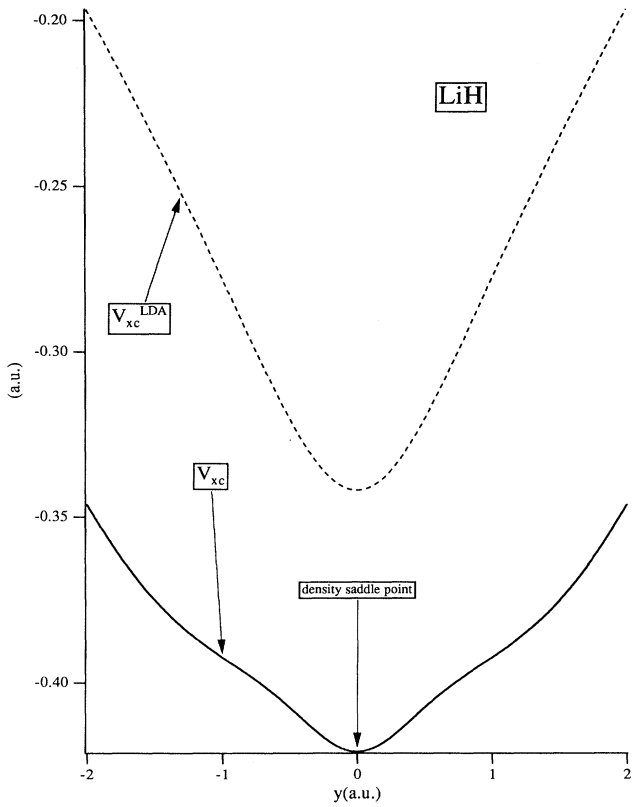

FIG. 4. Exchange-correlation potential and its LDA approximation along the axis perpendicular to the bond axis and going through the density saddle point.

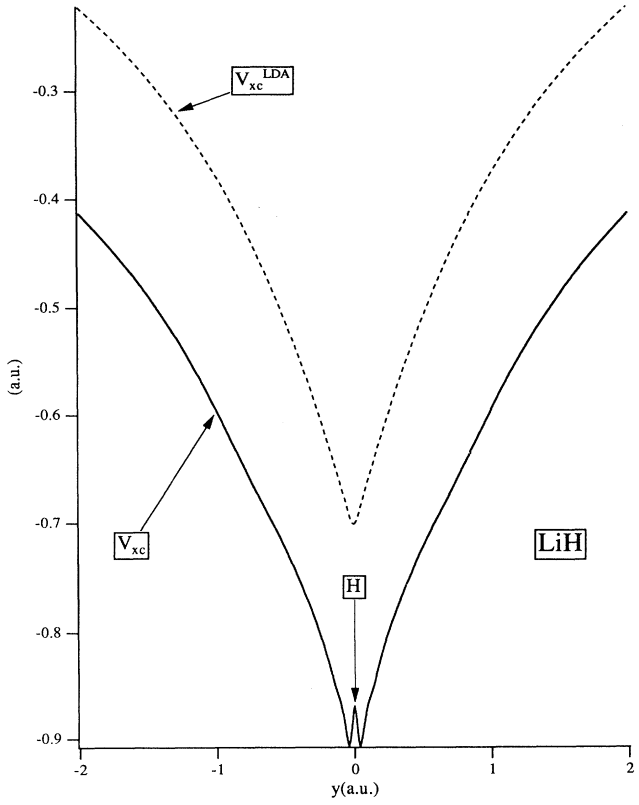

FIG. 5. Exchange-correlation potential and its LDA approximation along the axis perpendicular to the bond axis and going through the H nucleus.

v_{xc} is visibly smoothed out in LDA and v_{xc}^{LDA} lacks the proper long-range Coulombic asymptotics.

In Figs. 3–5 v_{xc} and v_{xc}^{LDA} are plotted along the axes going through the nuclei and the saddle point of ρ in the direction perpendicular to the bond axis. In all cases, apart from the above-mentioned countercusps at the nuclei, v_{xc} decreases monotonically with increasing distance y from the bond axis. One can see from Figs. 2 and 4 that at $z=-0.22$ a.u. and $y=0$ (the saddle point of ρ), v_{xc} also has a saddle point.

In conclusion, we have demonstrated that the procedure of Ref. [14], with some slight modification, is able to generate reasonably accurate KS exchange-correlation potentials in the general case of many-electron molecules. This opens the possibility to study these potentials for all the different types of bonding situations.

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